GEMINAL SYSTEMS.

19* REACTIONS OF AMINOMETHYLPHOSPHINES WITH ELECTROPHILIC REAGENTS

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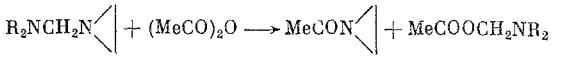
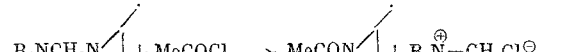
The order of the splitting of the geminal systems $\rangle N-C-X$, where X = N [2], O [3], S [4], etc., by electrophilic reagents is determined by the thermodynamic stability of the products formed. For example, in reactions (1) [5] and (2) [6] the attack of the acylating reagent is realized at the less basic nitrogen center, whereas in reactions of type (3) [3] it takes place at the still less basic oxygen:



(1)



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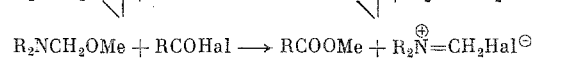
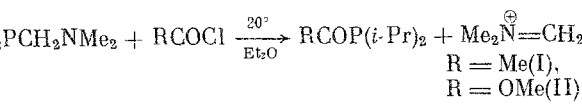


(3)

In the present work we studied the specificity of reactions of electrophilic reagents with geminal systems in the case of X = R_2P, i.e., aminomethylphosphines (AMP). As it turned out, when AMP's are reacted with acylating reagents, the attack of the latter takes place at the P atom with cleavage of the C–P bond and the formation of acylphosphines and methyleneimmonium salts†



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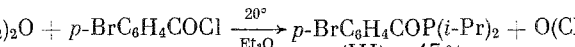

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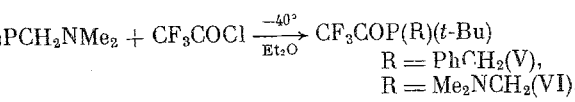
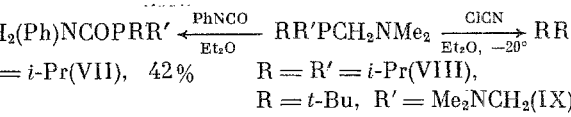


(7)

This method for the synthesis of acylphosphines was used for the optical activation of AMP's by reacting them with an insufficient quantity of a chiral acylating reagent in [7].

When AMP's are treated with phenyl isocyanate, the reagent is inserted into the C–P bond to form carbamoylphosphines, and under the action of ClCN AMP's are split to form cyanophosphines:



(8)

* For report 18 see [1].

†For the preliminary report see [7].

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TABLE 1. Constants of Acyl- and Cyanophosphines and Salts of AMP's

Compound	Yield, %	mp, °C	Found/calculated, %				
			C	H	N	P	Hal
t-Bu (Me_2NCH_2) PC (O) CF_3[a] (VI)	70	bp 55 (5mm)	–	–	–	–	–
(i-Pr)$_2$ PC (O) N (Ph) CH_2NMe_2[b] (VII)	42	–	–	–	–	–	–
t-Bu (Me_2NCH_2) PCN[c] (IX)	58	66 (1mm)	–	–	–	–	–
(i-Pr)$_2$ (Me) $\overset{\oplus}{P}CH_2$ $NMe_2I^{\ominus}$ (X)	89	133–135	–	–	4,16 / 4,42	9,55 / 9,78	–
(i-Pr)$_2$ (Me) $\overset{\oplus}{P}CH_2N$ $(CH_2)_3$ $CHCO_2MeI^{\ominus}$[d] (XI)	78	–	–	–	–	–	–
(i-Pr)$_2$ Me $\overset{\oplus}{P}CH_2N$ $(CH_2CH_2)_2$ $OI^{\ominus}$ (XII)	86	138–140	–	–	4,14 / 3,90	8,54 / 8,63	–
i-Pr ($PhCH_2$) $\overset{\oplus}{P}$ (Me) $CH_2N(CH_2CH_2)_2$ $OI^{\ominus}$ (XIII)	88	174–175	45,93 / 45,57	6,86 / 6,84	3,49 / 3,54	7,66 / 7,85	31,81 / 32,15
i-Pr (*t*-Bu) $\overset{\oplus}{P}$ (Me) CH_2N $(CH_2CH_2)_2OI^{\ominus}$ (XIV)	88	141–142	41,72 / 41,82	7,86 / 7,77	3,70 / 3,75	8,17 / 8,31	33,68 / 34,05
t-Bu (Ph) $PCH_2\overset{\oplus}{N}Me_3I^{\ominus}$ (XV)	81	192–193	45,76 / 45,78	7,05 / 7,35	3,73 / 3,81	8,44 / 8,45	34,78 / 34,60
t-Bu (Ph) $\overset{\oplus}{P}$ (Me) CH_2N $(CH_2CH_2)_2$ $OI^{\ominus}$ (XVI)		Experiment in NMR ampul					
(i-Pr)$_2\overset{\oplus}{P}$ (CH_2N $(CH_2CH_2)_2$ O)$_2$ $I^{\ominus}$ (XVII)	35	138–140	43,40 / 43,30	7,76 / 7,65	6,60 / 6,30	6,91 / 6,94	–
(i-Pr)$_2\overset{\oplus}{P}$ $Me_2I^{\ominus}$ (XVIII)	60	>190	35,41 / 35,03	7,21 / 7,30	–	11,01 / 11,31	46,12 / 46,35
(i-Pr)$_2$ $PCH_2\overset{\oplus}{N}Me_3$ $FSO_3^{\ominus}$ (XX)	62	138–141	41,27 / 41,52	8,76 / 8,65	4,72 / 4,85	–	–
(i-Pr)$_2$ $PCH\overset{\oplus}{N}(CH_2Ph)$ Me_2 $Br^{\ominus}$ (XXI)	67	142–143	56,25 / 55,40	8,34 / 8,40	4,59 / 4,05	–	–
i-Pr ($PhCH_2$) $PCH_2\overset{\oplus}{N}$ (CH_2Ph) Me_2 $Br^{\ominus}$ (XXII)	67	173–174	60,47 / 60,91	7,12 / 7,36	3,40 / 3,59	–	20,4 / 20,3
(–) *t*-Bu (Ph) $PCH_2\overset{\oplus}{N}(CH_2Ph)$ Me_2 $Br^{\ominus}$[e] (XXIII)	40	–	–	–	–	–	–
(i-Pr)$_2$ (Me) $\overset{\oplus}{P}CH_2\overset{\oplus}{N}Me_3$ $2Br^{\ominus}$ (XXIV)	23	115–120	–	–	–	–	–
(i-Pr)$_2$ (Me) $\overset{\oplus}{P}CH_2\overset{\oplus}{N}Me_3$ $2I^{\ominus}$ (XXV)	67	158–161	28,9 / 28,8	6,44 / 6,10	3,05 / 3,05	–	–
(i-Pr)$_2$ (Me) $\overset{\oplus}{P}CH_2\overset{\oplus}{N}Me_3FSO_3^{\ominus}I^{\ominus}$ (XXVI)	62	153–155	–	–	–	–	–
(i-Pr)$_2$ (Me) $\overset{\oplus}{P}CH_2\overset{\oplus}{N}$ (CH_2Ph) $Me_2Br^{\ominus}I^{\ominus}$ (XXVII)	58	125–127	41,81 / 41,70	6,55 / 6,60	3,17 / 2,85	5,85 / 6,35	–
(i-Pr)$_2$ P (O) $CH_2\overset{\oplus}{N}Me_3I^{\ominus}$ (XXVIII)	69	>250 (sublimation)	36,34 / 36,03	7,73 / 7,51	4,40 / 4,20	9,05 / 9,31	37,05 / 38,40
(i-Pr) ($PhCH_2$) $\overset{\oplus}{P}$ (H) Me $I^{\ominus}$ (XXIX)	91	>190	43,34 / 42,86	6,01 / 5,84	–	9,82 / 10,06	40,63 / 41,23

a) νCO 1685 cm^{-1}, M^+ 243 m/z.
b) νCO 1710 (1662 sh) cm^{-1}.
c) M^+ 172 m/z.
d) $[\alpha]_{546}^{20}$ –41.7° (C 5.75, MeOH).
e) $[\alpha]_{546}^{20}$ –3.39° (C 0.56, MeOH).

Thus, when AMP's, like other aminomethyl derivatives of N, O, and S [8], i.e., the elements closest to phosphorus in the periodic table, are split, the direction of the attack of the acylating reagent is determined by the thermodynamic stability of the methyleneimmonium salt formed. Judging from the comparative strength of the E–C bonds (kJ/mole) in Me_3N (393.6), MeOH (~381), Me_2S (305.6), Me_3P (276.3), and Me_3As (230.3) [9], we may postulate that aminomethylarsines should split according to a similar scheme [e.g., (4)].

TABLE 2. Nuclear-Magnetic-Resonance Spectra of Acyl- and Cyanophosphines and Salts of AMP's

Compound	Solvent	δ, ppm							J, Hz						
		Me_A	Me_B	Me—P	Me—N	CH_2—P	CH—P	other	Me_ACH	Me_BCH	Me_AP	Me_BP	CH_2P	Me—P	other
(VI)	$C_6D_5CD_3$				–	2,63 [a]	–	0,93 (t-Bu) 1,98 (MeN)	–	–	–	–	—	–	13,0 (*t*-BuP)
(VII)	$CDCl_3$	1,04	0,95		2,21	2,38	1,6	7,12 (Ph)	6,8	6,8	13,0	13,0	—	–	–
(IX)	Ph_2O [b]	–	–	–	2,04	2,76 Δν 20,0	–	0,98 (*t*-Bu)	–	–	–	–	—	–	5,6 (H_BP) 2,8 (H_AP), 13,1 (*t*-BuP) 12,8 (H_AH_B)
(X)	CD_3OD	1,29	1,29	1,80	2,37	3,44	2,66	–	7,0	7,0	16,8	16,8	5,0	13,0	–
(XI)	$CDCl_3$	1,41	1,41	2,0	–	4,06	–	3,10 m 3,75 (OMe)	7,0	7,0	17,0	17,0	—	12,0	–
(XII)	CD_3OD [c]	1,30	1,30	1,82	–	3,59	2,75	2,63 (CH_2N) 3,60 (CH_2O)	7,0	7,0	16,5	16,5	5,0	13,0	–
(XIII)	CD_3OD	1,12	1,12	1,80	2,57 (CH_2N) 3,62 (CH_2O)	3,81 (CH_2Ph)	2,70	7,45 (Ph)	7,0	7,0	17,0	17,0	—	13,0	14,0 (PCH_2Ph)
(XIV)	CD_3OD	1,38	1,33	1,86	2,65 (CH_2N) 3,60 (CH_2O)	3,52	2,85	1,35 (*t*-Bu)	7,0	7,0	16,5	16,5	5,5	12,8	15,0 (*t*-BuP)
(XV)	CD_3OD	–	–	–	3,19	4,27 Δν 43,2	–	1,02 (*t*-Bu) 7,69 (Ph)	–	–	–	–	—	–	14,0 (*t*-BuP) 15,0 (H_AH_B) 5,0 (H_AP), 3 0 (H_BP)
(XVI)	CD_3OD	–	–	2,18	2,62 (CH_2N) 3,50 (CH_2O)	3,81	–	1,08 (*t*-Bu) 7,52 (Ph)	–	–	–	–	—	13,0	15,0 (*t*-BuP)

TABLE 2. (continued)

Compound	Solvent	δ, ppm							J, Hz						
		Me_A	Me_B	Me—P	Me—N	CH_2—P	CH—P	other	Me_ACH	Me_BCH	Me_AP	Me_BP	CH_2P	Me—P	other
(XVII)	$CDCl_3$	1,46	1,46	–	–	3,85	3,00	2,72(CH_2N) 3,61(CH_2O)	7,0	7,0	16,0	16,0	4,5	–	–
(XVIII)	CD_3OD	1,26	1,26	1,79	–	–	2,68	–	7,0	7,0	17,5	17,5	—	13,0	–
(XIX)	CD_3OD	1,01	0,99	–	2,79	3,16	1,80	–	6,2	6,2	13,4	12,0	3,0	–	–
(XX)	$CDCl_3$	1,15	1,14	–	3,20	3,60	1,96	–	7,0	7,0	14,0	14,0	3,5	–	–
(XXI)	CD_3OD[d]	1,14	1,10	–	3,08	3,55	1,94	4,78(CH_2Ph) 7,60(Ph)	7,0	7,0	12,4	15,0	3,5	–	–
(XXII)	$CDCl_3$	1,16	1,24	–	2,71 (c.d.)	3,37	2,05	4,0(CH_2Ph) Δν 49,5 4,97(NCH_2Ph) 6,95; 7,37(Ph)	6,8	7,0	12,70	13,5	5,0	–	12,8(PCH_2Ph)
(XXIII)	CD_3OD			–	2,9 (c.d.)	4,20 Δν 36,0	–	1,05(*t*-Bu) 4,65(CH_2Ph) 7,5(Ph)	–	–	–	–	—	—	13,5(*t*-BuP) 15,0(H_AH_B) 5,0(H_AP), 2,5(H_BP)
(XXIV)	CD_3OD e	1,49	1,44	2,48	3,58	f	3,19	–	7,2	6,8	18,2	17,8	—	13,2	–
(XXV)	CF_3CH_2OHg	1,49	1,45	2,34	f	f	f	–	7,8	7,5	19,5	19,0	—	13,0	–
(XXVI)	CD_3OD	1,46	1,42	2,39	3,53	f	3,01	–	7,0	7,0	18,5	18,5	—	13,2	–
(XXVII)	D_2O[h]	1,85	1,76	2,76	3,75	f	3,43	5,23(CH_2Ph) 8,0(Ph)	6,9	6,9	18,5	18,5	—	13,2	–
(XXVIII)	CD_3OD	1,24	1,20	–	3,32	3,81	2,25	–	7,0	7,0	16,0	16,0	3,5	–	–
(XXIX)	CD_3OD	0,98	0,88	1,38	–	3,50	2,37	7,06(Ph)	7,0	7,0	19,5	19,5	—	14,0	14,5(PCH_2)

a) At −50°C, AB system, $\Delta\nu$=37.0 Hz, δ: 2.44 (H_A), 2.64 ppm (H_B); J_{H_AP}=3.2, $J_{H_AH_B}$=13.6, J_{H_ACF} <0.5, J_{H_BP}=1.5, J_{H_BCF}=1.5 Hz.

$\Delta G^{\neq}_{25}$=1.48 kcal/mole (60.97 kJ/mole), T_c=25°C.

b) The spectrum remains unchanged upon heating to 190°C.

c) $\delta^{31}P$ (CD_3OD) −40.8 ppm.

d) $\delta^{31}P$ (CD_3OD) +7.8 ppm.

e) $\delta^{31}P$ (CD_3OD) −39.1 ppm.

f) Signals overlap with solvent signals.

g) $\delta^{31}P$ [$(CF_3)_2C$=NOH] −40.4 ppm.

h) Values of δ relative to external reference.

In the reactions of AMP's with the alkylating reagent MeI, the electrophilic attack is also directed at the P atom:

$$RR'PCH_2X + MeI \xrightarrow[Et_2O]{20^\circ} RR'\overset{\oplus}{P}(Me)CH_2X\overset{\ominus}{I} \quad (9)$$
(X)—(XIV)

R = R′ = *i*-Pr, X = Me_2N— (X), 89%;
R = R′ = *i*-Pr, X = $MeO_2CCH(CH_2)_3N$— (XI), 78%;
R = R′ = *i*-Pr, X = $O(CH_2CH_2)_2N$— (XII), 86%;
R = *i*-Pr, R′ = $PhCH_2$, X = $O(CH_2CH_2)_2N$— (XIII), 88%;
R = *i*-Pr, R′ = *t*-Bu, X = $O(CH_2CH_2)_2N$— (XIV), 88%.

An increase in the steric hindrances at the P atom results in alkylation at the N atom:

$$t\text{-Bu(Ph)}PCH_2NMe_2 + MeI \xrightarrow[Et_2O]{20^\circ} t\text{-Bu(Ph)}PCH_2\overset{\oplus}{N}Me_3\overset{\ominus}{I} \quad (10)$$
(XV), 81%

However, when the basicity of the amino group in AMP's is lowered, alkylation again occurs at the P atom, although it is very slow (22 days):

$$t\text{-Bu(Ph)}PCH_2N(CH_2CH_2)_2O + MeI \xrightarrow[CD_3OD]{20^\circ} O(CH_2CH_2)_2NCH_2\overset{\oplus}{P}(Me)(t\text{-Bu})Ph\overset{\ominus}{I} \quad (11)$$
(XVI)

The reactions of AMP's with other alkyl iodides, i.e.,

$$(i\text{-Pr})_2PCH_2N(CH_2CH_2)_2O + RI \xrightarrow[Et_2O]{20^\circ} [(i\text{-Pr})_2(R)\overset{\oplus}{P}CH_2N(CH_2CH_2)_2O]\overset{\ominus}{I} \xrightarrow[-(i\text{-Pr}_2)PR]{+AMP} (i\text{-Pr})_2\overset{\oplus}{P}[CH_2N(CH_2CH_2)_2O]_2\overset{\ominus}{I} \quad (12)$$
R = Et(XVII), 35%;
R = $PhCH_2$(XVII), 30%

may be attributed to the primary attack of RI on the P atom followed by reaminomethylation at the P atom of the original AMP. Such conversions are known for diaminomethanes [8]. An attempt to insert a methylene group into the C—P bond of AMP XII under the action of CH_2N_2 yielded phosphonium salt XVIII, whose structure was confirmed by a back synthesis:

$$(XII) \xrightarrow[Et_2O,\ MeOH]{CH_2N_2} (i\text{-Pr})_2\overset{\oplus}{P}Me_2\overset{\ominus}{I} \xleftarrow[Et_2O]{MeI} (i\text{-Pr})_2PMe \quad (13)$$
(XVIII), 60%

When reacted with other electrophilic reagents under the same conditions, AMP's are alkylated and protonated at the N atom:

$$R_2PCH_2NMe_2 \begin{cases} \xrightarrow{HCl} R_2PCH_2\overset{\oplus}{N}(H)Me_2\overset{\ominus}{Cl} \\ \qquad R = i\text{-Pr}\ (XIX),\ 83\% \\ \xrightarrow[MeOSO_2F]{} R_2PCH_2\overset{\oplus}{N}Me_3FSO_3\overset{\ominus}{} \\ \qquad R = i\text{-Pr(XX)},\ 62\% \end{cases} \quad (14)$$

$$RR'PCH_2NMe_2 \xrightarrow[Et_2O,\ 20^\circ]{PhCH_2Br} RR'PCH_2\overset{\oplus}{N}(CH_2Ph)Me_2\overset{\ominus}{Br} \quad (15)$$

R = R′ = *i*-Pr(XXI), 67%; R = *i*-Pr, R′ = $PhCH_2$, 67%;
R = *t*-Bu, R′ = Ph (XXIII), 40%, $[\alpha]_{546}^{20}$ — 3,39° (*C* 0,56, MeOH)

With 1 mole of MeBr an AMP yields only bisquaternary salt XXIV. The additional alkylation of AMP monosalts X, XX, and XXI under the action of MeI also results in the formation of bisquaternary phosphonium—ammonium salts XXV—XXVII:

$$(i\text{-Pr})_2PCH_2NMe_2 + MeBr \rightarrow (i\text{-Pr})_2(Me)\overset{\oplus}{P}CH_2\overset{\oplus}{N}Me_3 2\overset{\ominus}{Br} \quad (16)$$
(XXIV), 23%

$$(X) + MeI \rightarrow i\text{-Pr}_2(Me)\overset{\oplus}{P}CH_2\overset{\oplus}{N}Me_3 2\overset{\ominus}{I} \quad (17)$$
(XXV), 67%

$$(XX),\ (XXI) + MeI \rightarrow (i\text{-Pr})_2(Me)\overset{\oplus}{P}CH_2\overset{\oplus}{N}(R)Me_2Hal\overset{\ominus\ominus}{I} \quad (18)$$

R = Me; Hal = $FSO_3^{\ominus}$ (XXVI), 62%; R = $PhCH_2$, Hal = $\overset{\ominus}{Br}$
(XXVII), 58%.

Naturally, an AMP oxide is alkylated under the action of MeI at the nitrogen atom:

$$(i\text{-Pr})_2P(O)CH_2NMe_2 + MeI \xrightarrow[Et_2O]{20^\circ} (i\text{-Pr})_2P(O)CH_2\overset{\oplus}{N}Me_3\overset{\ominus}{I} \quad (19)$$
(XXVIII), 69%

The structures of the compounds obtained (Table 1) were confirmed by their NMR spectra. In the PMR spectra of the aminomethylphosphonium salts the signal of the CH_3 group introduced is displayed in the form of a doublet, which is similar with respect to its chemical shift and value of J (HCP) to the signal of a known phosphonium salt, for example, XXIX (Table 2). In the case of methylation at the N atom, the spectrum of the ammonium salt shows an increase in the intensity of the signal of MeN and a downfield shift (> 3 ppm) relative to the original AMP [7] and the monophosphonium salt (~2.0-2.3 ppm, see also the spectrum of the known ammonium salt XXVIII in Table 2). Another spectral test for a phosphonium structure as opposed to an ammonium structure is the significantly greater downfield shift of the signal of HC, i.e., the isopropyl substituent* (see Table 2). The ^{31}P NMR spectra provided additional confirmation of the aminomethylphosphonium structure of XII ($\delta\ ^{31}P - 40.8$ ppm) and the phosphinomethylammonium structure of XXI ($\delta\ ^{31}P + 7.8$ ppm). The value of ^{31}P for XII is characteristic of tetracoordinate P in phosphonium salts [10, 11] and practically coincides with the chemical shifts of bisquaternary salts XXIV and XXV; the chemical shift of monoammonium salt XXI is characteristic of tricoordinate P in AMP's [7] and phosphines [10, 11].

The dual reactivity of AMP's under consideration cannot be attributed to the different responses of amines and phosphines to the alkylating reagents, since the competitive reactions of equimolar mixtures of Et_3N and Et_3P with MeI or $PhCH_2Br$ in ether at 20°C give the same result, i.e., the preferential formation of the phosphonium salt over the ammonium salt in a 7:1 ratio. An exclusively phosphonium salt was previously obtained in a similar reaction during a comparison of the nucleophilic properties of tertiary phosphines and amines with various electrophiles, particularly with MeI [12]. It should also be noted that in a study of the alkylation of AMP's with a highly basic amine component under the action of MeI in CD_3OD by the PMR method (the experiment in an NMR ampul), we discovered that the reaction takes place at the N and P atoms. From the ratio between the intensities of the signals of the ammonium and phosphonium salts formed it follows that the alkylation is three times faster at the P atom than at the N atom. The use of $PhCH_2Br$ as an electrophile under the same conditions results in the formation of only an ammonium salt. In the case of AMP's with a weakly basic amine component, an exclusively phosphonium salt is formed in the reaction with MeI, and in the reaction with $PhCH_2Br$ a mixture of unidentified products is formed.

EXPERIMENTAL

The NMR spectra were measured on a Tesla BS-487 spectrometer (^1H, 80 MHz, relative to the internal reference HMDS), a JNM-C-60-HL spectrometer (^{19}F, 56.546 MHz, relative to the external reference CF_3CO_2H), and a JNM-4H-100 spectrometer (^{31}P, 40.5 MHz, relative to the external reference 85% H_3PO_4). The ampuls were filled in an argon atmosphere, and the concentration of the samples was ~15%. The IR spectra of the pure liquids were measured on a UR-20 spectrometer in KBr cuvettes. All the syntheses and physicochemical investigations of the compounds of trivalent phosphorus were carried out without the access of air or moisture to the argon atmosphere. The glass system was evacuated (1 torr), heated by the flame of a burner, and filled with dry argon. Only absolute solvents and freshly redistilled reagents were used in the work. The synthesis of the original AMP's and compounds II, XIX, XXIII, and XXVIII was described in [7], that of acylphosphine I was described in [13], and that of acylphosphines III-V and cyanophosphine VIII was described in [14]. The constants, elemental analysis, and NMR spectra are given in Tables 1 and 2.

Trifluoroacetyl(dimethylaminomethyl)-tert-butylphosphine (VI). a) Bis(dimethylaminomethyl)-tert-butylphosphine. The reaction of 2.31 g (25.6 mmole) of t-$BuPH_2$ (which was obtained by reducing t-$BuPCl_2$ with $LiAlH_4$ in dibutyl ether, bp 54°C) and 5.4 g (53 mmole) of bisdimethylaminomethane according to [7] yielded 3.29 g (63%) of a colorless liquid, bp 50°C (0.5 torr), M^+ 204 m/z. PMR spectrum (C_6H_6, δ, ppm, J, Hz): 0.94 (Me_3C, $^3J_{HCP}$ = 11.0), 2.35 (CH_2, $\Delta\nu$ = 21.3 Hz, $^2J_{HP}$ = 2.25, $^2J_{HH}$ = 13.0).

b) A 1.2-g portion (8.8 mmole) of CF_3COCl was bubbled through a solution of 1.8 g (8.8 mmole) of $(Me_2NCH_2)_2P(t\text{-Bu})$ in 35 ml of ether at −40°C. The temperature of the mixture was brought up to 20°C, the precipitate was separated, the ether was removed from the filtrate, and the residue was vacuum-distilled. This yielded 1.5 g (70%) of VI, lemon yellow liquid.

* The observed spectral anomaly, i.e. the absence of inequivalence of the methyl protons of the i-Pr substituent in aminomethylphosphonium salts X-XIV, will be considered in the next report.

Phenylcarbamoyldimethylaminomethyldiisopropylphosphine (VII). A solution of 0.6 g (5.0 mmole) of PhNCO in 10 ml of ether was given an addition of 0.88 g (5.0 mmole) of $Me_2NCH_2P(i\text{-}Pr)_2$ in 10 ml of ether, the mixture was held for 2 h, and the solvent was removed. This yielded 0.63 g (42%) of VII, lemon yellow liquid.

Reaction of Dimethylaminomethylisopropyl-tert-butylphosphine [15] with BrCN. A solution of 0.9 g (4.7 mmole) of the AMP in 10 ml of ether was given an addition with stirring of a solution of 0.5 g (4.7 mmole) of BrCN in 5 ml of ether at 20°C. After 1 h, the precipitate was separated, the ether was removed from the filtrate, and the residue was vacuum-distilled. This yielded 0.46 g of a colorless liquid, bp 59°C (3 torr), which according to its mass spectrum is a mixture of i-Pr(t-Bu)PCN, M^+ 157 m/z, and i-Pr(t-Bu)PBr, M^+ 210/212 m/z.

Dimethylaminomethyl-tert-butylcyanophosphine (IX). A 0.7-g portion (11.4 mmole) of ClCN was bubbled through a solution of 1.9 g (9.3 mmole) of $(Me_2NCH_2)_2P(t\text{-}Bu)$ in 20 ml of ether at −30°C. The mixture was brought up to 20°C. After 2 h, the copious precipitate was separated, the ether was removed from the filtrate, and the residue was vacuum-distilled. This yielded 0.87 g (58%) of IX, colorless liquid.

Dimethylaminomethyldiisopropylmethylphosphonium Iodide (X). A solution of 1.02 g (7.2 mmole) of MeI in 5 ml of ether was added to a solution of 1.26 g (7.2 mmole) of dimethylaminomethyldiisopropylphosphine in 20 ml of ether. The precipitate formed was filtered, washed three times with ether, and dried in a vacuum. Recrystallization from an MeOH–ether mixture yielded 2.02 g (89%) of white crystals of X.

S-(−)-Methyl Ester of N-Prolinomethyldiisopropylmethylphosphonium Iodide (XI). In a similar manner 0.89 g (78%) of XI in the form of yellowish crystals with $[\alpha]_{546}^{20}$ −41.7° (c 5.75, MeOH) was obtained from 0.73 g (2.9 mmole) of the S-(−)-methyl ester of N-prolinomethyldiisopropylphosphine and 0.4 g (2.9 mmole) of MeI in 15 ml of ether.

N-Morpholinomethyldiispropylmethylphosphonium Iodide (XII). In a similar manner 0.74 g (88%) of XII in the form of white acicular crystals was obtained from 0.5 g (2.3 mmole) of N-morpholinomethyldiisopropylphosphine and 0.33 g (2.3 mmole) of MeI in 10 ml of ether.

N-Morpholinomethylisopropylbenzylmethylphosphonium Iodide (XIII). In a similar manner 0.25 g (88%) of XIII in the form of white acicular crystals was obtained from 0.2 g (0.75 mmole) of N-morpholinomethylisopropylbenzylphosphine and 0.11 g (0.77 mmole) of MeI in 10 ml of ether after 12 h.

N-Morpholinomethylisopropyl-tert-butylmethylphosphonium Iodide (XIV). In a similar manner 0.67 g (88%) of XIV in the form of white acicular crystals was recovered from 0.47 g (2.03 mmole) of N-morpholinomethylisopropyl-tert-butylphosphine [15] and 0.29 g (2.04 mmole) of MeI in 20 ml of ether after crystallization from a CCl_4–MeOH–ether mixture.

tert-Butylphenylphosphinomethyltrimethylammonium Iodide (XV). A solution of 0.2 g (0.9 mmole) of dimethylaminomethyl-tert-butylphenylphosphine in 5 ml of ether was given an addition of a solution of 0.15 g (1.06 mmole) of MeI in 10 ml of ether at 20°C. After 12 h the precipitate was separated, washed with ether, dried, dissolved in MeOH, and frozen out. This yielded 0.28 g (81%) of XV.

Bis(N-morpholinomethyl)diisopropylphosphonium Iodide (XVII). A solution of 1.45 g (6.3 mmole) of N-morpholinomethyldiisopropylphosphine in 10 ml of ether at 20°C was given an addition of a solution of 1.04 g (6.7 mmole) of EtI and left to stand overnight. The precipitate was filtered, washed with ether, and crystallized from an MeOH–ether mixture. This yielded 0.51 g (35%) of XVII in the form of white plates. Compound XVII was also obtained from 1.1 g (4.8 mmole) of the same AMF and 1.08 g (4.8 mmole) of $PhCH_2I$.

Dimethyldiisopropylphosphonium Iodide (XVIII). a) A solution of 0.52 g (1.44 mmole) of XII in 10 ml of MeOH was given an addition of an ethereal solution of CH_2N_2 to a persistent yellow color. Evolution of a gas was observed. The mixture was held for 0.5 h, the excess CH_2N_2 and solvent were removed, and the residue was recrystallized from an MeOH–ether mixture. This yielded 0.25 g (60%) of XVIII in the form of yellowish crystals.

b) A solution of 1.2 g (9.1 mmole) of $(i\text{-}Pr)_2PMe$ in 10 ml of ether was given an addition of 1.5 g (10.6 mmole) of MeI in 5 ml of ether. The precipitate was separated, washed with ether, and recrystallized from an MeOH–ether mixture. This yielded 1.5 g (60%) of XVIII in the form of white crystals which yellow during storage.

Diisopropylphosphinomethyltrimethylammonium Fluorosulfonate (XX). A solution of 1.1 g (6.3 mmole) of dimethylaminomethyldiisopropylphosphine in 15 ml of ether was given an addition of a solution of 1.3 g (11 mmole) of $MeOSO_2F$ in 5 ml of ether at −40°C. The precipitate was separated, washed three times with ether, and dried in a vacuum. This yielded 1.1g (62%) of XX in the form of white crystals which deliquesce in air.

Diisopropylphosphinomethyldimethylbenzylammonium Bromide (XXI). In a similar manner 1.65 g (67%) of XXI in the form of white crystals, which yellow during storage, was obtained from 1.26 g (7.2 mmole) of the same AMP and 1.23 g (7.2 mmole) of $PhCH_2Br$ in 20 ml of ether at 20°C after crystallization from an MeOH–ether mixture.

Isopropylbenzylphosphinomethyldimethylbenzylammonium Bromide (XXII). In a similar manner 0.42 g (67%) of XXII in the form of white prismatic crystals was obtained from 0.33 g (1.5 mmole) of dimethylaminomethylisopropylbenzylphosphine and 0.26 g (1.5 mmole) of $PhCH_2Br$.

Trimethylammoniomethyldiisopropylmethylphosphonium Dibromide (XXIV). A solution of 1.2 g (6.9 mmole) of dimethylaminomethyldiisopropylphosphine in 20 ml of ether was given an addition of a solution of 0.6 g (6.7 mmole) of MeBr in 10 ml of ether at −20°C. The precipitate was separated by decantation, dried in a vacuum, and recrystallized from MeCN. This yielded 0.57 g (23%) of XXIV) in the form of white crystals, which yellow during storage.

Trimethylammoniomethyldiisopropylmethylphosphonium Diiodide (XXV). A solution of 0.52 g (6.4 mmole) of X in 30 ml of MeCN was given an addition of an excess of MeI. After 12 h the crystalline product was filtered out, washed twice with MeCN, and dried in a vacuum. This yielded 0.5 g (67%) of XXV in the form of acicular crystals.

Trimethylammoniomethyldiisopropylmethylphosphonium Fluorosulfonate Iodide (XXVI). In a similar manner 0.28 g (62%) of XXVI in the form of white crystals was obtained from 0.33 g (1.1 mmole) of XX and 0.2 g (1.8 mmole) of MeI.

Dimethylbenzylammoniomethyldiisopropylmethylphosphonium Bromide Iodide (XXVII). In a similar manner 0.42 g (58%) of XXVII in the form of white rhombic crystals, which yellow during storage, was obtained from 0.52 g (1.5 mmole of XXI and 0.5 g (3.5 mmole) of MeI.

Methylisopropylbenzylphosphonium Iodide (XXIX). A solution of 0.5 g (3.0 mmole) of i-$Pr(CH_2Ph)PH$ was treated with an excess of MeI in 20 ml of ether. Recrystallization from an MeOH–ether mixture yielded 0.84 g (91%) of XXIX, white crystals.

Reaction of Et_3N and Et_3P with MeI. A solution of 0.62 g (6.0 mmole) of Et_3N and 0.72 g (6 mmole) of Et_3P in 35 ml of ether was given an addition of 0.87 g (6 mmole) of MeI. The mixture was left to stand overnight, and the precipitate was separated, washed with ether, and dried. This yielded 1.5 g of a substance. According to the PMR spectrum ($CHCl_3$), it is a mixture of $Et_3\overset{\oplus}{P}MeI^{\ominus}$ and $Et_3\overset{\oplus}{N}MeI^{\ominus}$ in a 7:1 ratio. $Et_3\overset{\oplus}{P}MeI^{\ominus}$, δ, ppm: 1.31 ($\underline{Me}CH_2$), 2.1 (MeP), 2.55 ($CH_2P$), J_{MeCH_2P} = 18.0, J_{HH} = 7.0, J_{MeP} = 13.5, $J_{Me\underline{C}H_2P}$ = 13.0 Hz. $Et_3\overset{\oplus}{N}MeI^{\ominus}$, δ, ppm: $\underline{Me}CH_2$ overlapped by the $\underline{Me}\overline{CH_2}$ signal of the phosphonium salt, 3.22 (MeN), 3.58 (CH_2N), J_{HH} = 7.0 Hz.

Reaction of Et_3N and Et_3P with $PhCH_2Br$. A solution of 0.14 g (12 mmole) of Et_3P and 0.234 g (23 mmole) of Et_3N in 30 ml of ether was given an addition of 0.207 g (12 mmole) of $PhCH_2Br$, and the mixture was left to stand overnight. The precipitate was filtered, washed with ether, and dried. This yielded 0.2 g of a substance. According to the PMR spectrum ($CDCl_3$), it is a mixture of the salts $Et_3\overset{\oplus}{P}CH_2PhBr^{\ominus}$ and $Et_3\overset{\oplus}{N}CH_2PhBr^{\ominus}$ in a 7:1 ratio. $Et_3\overset{\oplus}{P}CH_2PhBr^{\ominus}$, δ, ppm: 1.05 (Me), 2.42 (CH_2P), 4.2 (CH_2Ph), J_{HH} = 7.0, J_{MeP} = 18.0, J_{CH_2P} = 13.0, J_{PCH_2Ph} = 15.0 Hz. $Et_3\overset{\oplus}{N}CH_2OhBr^{\ominus}$, δ, ppm: 1.12 (Me), 3.30 (CH_2N), 4.72 (CH_2Ph), J_{HH} = 7.0 Hz.

CONCLUSIONS

1. In the reactions of aminomethylphosphines with the acylating reagents RCOCl, ClCN, and PhNCO the electrophilic attack is carried out at the phosphorus atom with cleavage of the C–P bond and the formation of acyl-, cyano-, and carbamoylphosphines.

2. Aminomethylphosphines display dual reactivity with respect to alkylating reagents. The attack of MeI is directed at the phosphorus atom to form aminomethylphosphonium salts, where as $PhCH_2Br$, $MeOSO_2F$, and HCl react at the nitrogen atom, producing phosphinomethylammonium salts. The regiospecificity of the reaction depends on the basicity of the N atom, the size of the substituents on the P atom, and the type of alkylating reagent.

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REACTION OF N-ACETOXYMETHYLACETAMIDE AND N-ACETOXYMETHYLBENZAMIDE WITH ESTER–AMIDES AND AMIDES OF PHOSPHOROUS ACID

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As a continuation of our investigations of the reactions of ester–amides and amides of the acids of trivalent phosphorus we studied the reactions of N-acetoxymethylacetamide (I) and N-acetoxymethylbenzamide (II) with diethyl diethylamidophosphite (III), ethyl tetraethyldiamidophosphite (IV), and hexaethyltriamidophosphite (V) for the purpose of ascertaining the influence of the nature of the substituent on the N atom in the electrophilic reagent on the direction of the substitution reactions. The presence of two nucleophilic centers and the ambidentate nature of the P^{III}–N bond in amidophosphites [1] allows us to expect the formation of products either at the P atom or at an N atom, depending on the structure of the electrophilic reagent.

It has previously been shown that the reactions of mono-, di-, and triamidophosphites III–V with N-hydroxymethyl derivatives of phenol [2] and benzamide [3] result in the simultaneous formation of products of both types, while N-hydroxymethylphthalimide reacts only at the N atom [3]. N-Acetoxy- and chloromethyldiethylamine react with III, IV, and V only at the P atom to form quasi-phosphonium salts or the corresponding phosphonates [4-6]. In ether and other solvents I and II react with triamidophosphites to form the quasi-phosphonium salts tris(deithylamino)(acetamidomethyl)- and tris(diethylamino)(benzamidomethyl)phosphonium acetate, respectively (VI and VII) [7].

In the present work we studied the reactions of I and II with III through V without a solvent upon heating. The composition of the reaction mixtures was monitored by ^{31}P NMR. The samples were held in ampuls under cooling before the spectra were recorded.

It was shown that the reaction of I with V results in the formation of tris(diethylamino)(acetamidomethyl)-phosphonium acetate (VI) (δ 54 ppm, yield equal to 73.2%) and tetraethyldiamidoacetoxyphosphite (VIII) (δ 126 ppm, yield equal to 12.5%). Their simultaneous formation was detected spectrally. The constants of VIII are

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